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METHOD OF PHOTOCHEMICAL CATALYTIC DEGREDATION OF COMPLEX-FORMING SUBSTANCES
[ZPŮSOB FOTOCHEMICKÉ KATALYTICKÉ DEGRADACE KOMPLEXOTVORNÝCH LÁTEK]

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This invention pertains to a method of photo-oxidation degradation of complex-forming substances with an acid or an acid and an initiating hydrogen peroxide additive in the presence of ions of iron, copper and nickel as photocatalysts. /1[*]

In recent years, photochemical processes have been finding application in treatment of wastewater. This refers specifically to photo-oxidation degradation that makes use of experience with the thermal reactions of hydrogen peroxide and water purification with UV radiation. The inventors of some photochemical processes for treating waste water (Clarke W., Knowles, G.: *Effluent Water Treat. J.*, 22, 335, 1982; Lipowicz, M.: *Chemical Eng.* 88, 40, 1981) that utilize hydrogen and/or oxygen as an oxidizing agent believe that this will bring about a drop in the levels of organic carbon by as much as 4% of the original quantity; Peterson and Zaleiko (*Water Eng. Manag.*, 128, 32, 1981, *CA*: 96, 11202a) note that photochemical purification using hydrogen peroxide as the oxidizing agent have resulted in purification levels of up to 99.9% in some types of wastewater.

Compounds that form solid complexes with a number of metal ions also occur in wastewater from industrial processes. Metals bound in complexes generally cannot be removed from solutions by means of standard chemical processes during the treatment of these wastewaters and are the reason for the escape of metal ions into the waste flows.

[*] Numbers in the margin indicate pagination in the foreign text.

On the other hand, if we are talking about discharges of wastewaters that contain free complexation agents into the water flow, the sludge that contains the metals, including heavy metals in an insoluble form generally leads to re-introduction of the metals into solution and to secondary contamination of the water flow when these substances come into contact with the sediment.

Rinse water from galvanic baths that contain a number of complexation substances and ions of heavy metals constitute a special case of wastewater (Fuka, T., et al.: *Technická práce* [*Technical Operations*], 36, 3, 22, 1984). Treatment of these wastewaters is a significant ecological problem. The proposed invention offers a solution to this problem.

The basis of the invention consists of the photocatalytic oxidation degradation of several complexation agents such as the disodium salt of ethylenediamine tetra-acetic acid, the sodium salt of sodium N, N-methyldithiocarbamate, sodium benzoate and phenol with use of oxygen (air) as the oxidation agent. Aqueous solutions of the complexation agents are irradiated with UV-VIS [Ultra-violet and Visible light] radiation, which is emitted by an intermediate pressure Hg vapor lamp with the simultaneous bubbling through of oxygen (air) in the presence of ions of iron, copper or nickel in the form of soluble inorganic salts in catalytic concentrations, i.e., at least 17 mg/liter. In some cases, adding hydrogen peroxide to the solution undergoing irradiation and bubbling in a concentration cor-

responding to a 1/10 molar concentration of the complex-forming substances during the initial phase of degradation is advisable.

The method of photochemical degradation based on the invention is illustrated by examples of its practical implementation. The concentration of complex-forming substance was selected so that it corresponds to the upper limits of concentration for the given substance /2 in wastewater, that is, to maximum contamination.

Example 1

Complexone III in the amount of 1.49 grams dissolved in 4,000 ml of water, which corresponds to the upper limit of concentration in rinse water from galvanic processes, was placed in a quartz photochemical reactor. Sixty seven (67) mg of Fe^{2+} was added to the solution in the form $(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O$. The reaction mixture was bubbled through with oxygen which was applied over fritted glass and also supported by active mixing of the solution. The reaction solution was irradiated with the entire spectrum of an RVK 400 W mercury vapor lamp placed in a water-cooled quartz sleeve. The temperature of the reaction solution was maintained at 28°C. Time of irradiation was 240 minutes. Specimens were collected at 60-minute intervals and analyzed using the manganometric titration method. After 60 minutes, 0.86 grams of the complexone, that is. 57.6% had been broken down.

Example 2

Cupral (sodium N,N-diethyldithiocarbamate) in an amount of 0.90 grams, which corresponds to the upper limit of concentration in the rinse water from galvanic processes, was placed in a quartz photochemical reactor together with 67 mg Fe^{2+} and dissolved in 4,000 ml of water. The process was then carried out as in Example 1. The course of degradation for the cupral during irradiation was monitored spectrophotometrically. After 120 minutes of irradiation, 0.62 grams of the cupral, or 69.2%, had been broken down.

Example 3

Cupral in an amount of 0.90 grams, which corresponds to the upper limit of concentration in the rinse water from galvanic processes, was placed in a quartz photochemical reactor together with 76 mg of Cu^{2+} in the form of $CuSO_4$ and dissolved in 4,000 ml of water. The process was then carried out as in Example 1. The course of breaking down the cupral during radiation was monitored spectrophotometri-cally. After 120 minutes of irradiation, 0.73 grams of the cupral, or 90.1%, had been broken down.

Example 4

Cupral in the amount of 0.90 grams, which corresponds to the upper limit of concentration in rinse water from galvanic processes, was placed in the quartz photochemical reactor together with 76 mg of Cu^{2+} in the form of $CuSO_4$ and dissolved in 4,000 ml of water. Prior to the start of radiation, hydrogen peroxide in the amount of 0.136

grams was added to the solution to initiate the beginning stage of the reaction. From this point, the process was carried out as in Example 2. After 60 minutes of irradiation, 0.71 grams of the cupral, or 79.3%, had broken down.

Example 5

Sodium benzoate in an amount of 0.58 grams, which corresponds to the upper limit of concentration in rinse water from galvanic processes, was placed in a quartz photochemical reactor together with 67 mg of Fe^{2+} in the form of $(NH_4)_2Fe(SO_4)_2$ and dissolved in 4,000 ml of water. The process then proceeded in accordance with Example 1. The course of breakdown of the sodium benzoate was monitored by means of high-pressure liquid chromatography. After 60 minutes of radia- /3 tion, 0.12 grams, that is, 20.7%, of the sodium benzoate had been broken down.

Example 6

Phenol in an amount of 0.38 grams, which corresponds to the upper limit of concentration in rinse water from galvanic processes, was placed in a quartz photochemical reactor together with 67 mg of Fe^{2+} in the form of $(NH_4)_2Fe(SO_4)_2$ and dissolved in 4,000 ml of water. The process then proceeded in accordance with Example 1. The course of phenol breakdown during irradiation was monitored by means of high-pressure liquid chromatography. After 60 minutes of radiation, 0.33 grams of the phenol, that is 88.4%, had broken down.

Example 7

Phenol in the amount of 0.38 grams was placed in a quartz photochemical reactor together with 67 mg of Fe^{2+} in the form of $(NH_4)_2Fe(SO_4)_2$ and dissolved in 4,000 ml of water. Prior to starting the radiation, hydrogen peroxide in the amount of 0.136 grams, which initiates the beginning stage of the reaction, was added. The process then proceeded in accordance with Example 1. The course of phenol breakdown was monitored by means of high-pressure liquid chromatography. After 30 minutes of radiation, 0.33 grams, that is, 88%, of the phenol had been broken down.

Example 8

Oxalic acid in the amount of 0.74 grams was placed in a quartz photochemical reactor together with 45.7 mg of Fe^{2+} in 90 ml of water. The reaction solution was then irradiated with the entire spectrum of an RVL125W intermediate pressure mercury vapor lamp, which was placed centrally in a water-cooled sleeve. Mixing was ensured by a current of oxygen that was added over fritted glass. Temperature of the reaction mixture was maintained at 25°C. The time of radiation was 150 minutes. Specimens were collected at intervals of 30 minutes and analyzed by manganometric titration. After 30 minutes of radiation, 0.44 grams, or 58.8% of the oxalic acid had been broken down.

Example 9

Oxalic acid in the amount of 0.74 grams was placed in a quartz photochemical reactor together with 52 mg of Cu^{2+} in the form of $CuSO_4$

in 90 ml of water. The process then proceeded in accordance with Example 8. After 30 minutes of radiation, 0.26 grams of oxalic acid, that is, 34.4%, had been broken down.

Example 10

Oxalic acid in the amount of 0.73 grams was placed in a quartz photochemical reaction together with 48 mg Ni^{2+} in the form of $NiSO_4$ in 90 ml of water. The process was then carried out in accordance with Example 8. After 30 minutes of irradiation, 0.14 grams of the oxalic acid, that is, 19.1%, had broken down.

CLAIMS OF THE PATENT

The method of photochemical catalytic degradation of complex-forming substances from the group that includes the disodium salt of /4 ethylenediamine tetra-acetic acid, the sodium salt of N,N-diethyl-dithiocarbamate, sodium benzoate and phenol in an aqueous solution or in wastewater *is distinguished by the fact* that the complex-forming substances or mixtures of them in an aqueous solution in waste water are exposed to the effects of ultra-violet radiation and visible light with oxygen or air bubbled through them simultaneously with the addition of ions of iron, copper or nickel in a concentration of at least 17 mg/liter at laboratory temperatures with the benefit of hydrogen peroxide, which is added at the start of the reaction in a concentration that corresponds to a 1/10 molar concentration of the complex-forming substances.